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DEPARTMENT OF PHYSICS, B-019
LA JOLLA, CALIFORNIA 92093

Physics FAX 619-534-0173

October 6, 1989

Dr. George Wright, Code 1114SS
Detail, Solid State Electronics
Department of the Navy
Office of the Chief of Naval Research
800 North Quincy Street
Arlington, Virginia 22217-5000

Subject: ONR-N00014-87-K-0338, UCSD, S. Schultz, Principal Investigator

(1) Annual Letter Report, 11/1/88 - 10/31/89
(2) Publications/Patents/Presentations/Honors Report, 11/1/88-10/31/89
(3) Cumulative bibliography 5/1/87 - 10/31/89 (with #4 preprint, " note of significance of paper" attached)
(4) Final Technical Report - Cumulative - 5/1/87 - 10/31/89
(5) reprint: Sol. St. Commun. 70, #12, 1159 (1989), Oseroff, et al., "Observation of complex magnetic behavior in the Perovskite rare earth copper oxide systems, R_2CuO_4".
preprint: Phys. Rev. B (1989), Oseroff, et al., "Magnetization, EPR, microwave absorption and specific heat in rare earth copper oxides, R_2CuO_4".

Dear George:

I am enclosing herewith 2 copies each of the above referenced reports, along with one copy each of the 1 reprint and 1 preprint. As to an IBM disk with Word Perfect 5.0, we do not have the 5.0 on campus as yet, and our own Department is virtually totally MacIntosh oriented. We are enclosing a disk with MacWrite 4.6 should it turn out it is needed, and in the interim we will try to locate a Word Perfect 5.0 if that is necessary.

Best regards to Kristl.

Sincerely,

Sheldon Schultz

/jbw

Enclosures

ANNUAL LETTER REPORT
N00014-87-K-0338
For Period 1 November 1988 to 31 October 1989
Sheldon Schultz, Principal Investigator
University of California, San Diego

In the prior technical reports we have discussed that we are working on two problems. The first, is to implement a new approach we have suggested to utilize electron paramagnetic resonance (EPR) as a probe of electron transport across the silicon-metal interface. The second is an investigation of important properties of the copper-oxide high T_c superconductors.

With respect to the first problem, in prior reports we have discussed how we have made the special P-doped silicon samples required, developed techniques for maintaining an atomically clean silicon surface in UHV without high temperature processing, and finally provided the proof of concept for samples made in UHV but, of necessity, measured in a separate EPR apparatus. These experiments validated our original concept that we would develop a dedicated UHV system with in-situ EPR capability to perform the definitive experiments. For the past year we have been constructing this apparatus, and it is now nearing completion. We have also made additional samples, and completed a detailed Auger analysis which confirms our preliminary results that there is a significant difference in the electron coupling between Ag and the other metals studied (Cu, Au, or Al). Professor Lu Sham and Dr. V. Gomez have initiated a theoretical study motivated both by these results, and in anticipation of those to come, from the new apparatus.

With respect to the investigation of copper-oxide superconductivity, we have completed detailed investigations into the magnetic properties of single crystals of the family R_2CuO_4 (R = Pr, Nd, Sm, Eu, or Gd). This system has been shown to become superconducting when doped with Ce or Th. It is particularly interesting because the Cu-O is purely planar and is claimed to have electron conductivity. We describe the complex magnetic behavior observed, which includes antiferromagnetic transitions, weak ferromagnetism, anomalous anisotropy, spin canting , and spontaneous spin reorientation in the preprint enclosed, (Oseroff, et al.), which has been accepted for publication by Physical Review.

OFFICE OF NAVAL RESEARCH

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

FOR

1 NOVEMBER 1988 - 31 OCTOBER 1989

FOR

CONTRACT NOOO14-87-K-0338

R&T NO. 414M013---01/87 FEB 18 (1114SS)

A NEW APPROACH TO UNDERSTANDING THE SEMICONDUCTOR SURFACE AND INTERFACES

DR. SHELDON SCHULTZ, PRINCIPAL INVESTIGATOR

UNIVERSITY OF CALIFORNIA, SAN DIEGO

DEPARTMENT OF PHYSICS, B-019

LA JOLLA, CALIFORNIA 92093

Report 1 November 1988 through 31 October 1989

a. Papers submitted to refereed Journals (and not yet published):

Oseroff, S.B., Rao, D., Wright, F., Vier, D.C., Schultz, S., Thompson, J., Fisk, Z., Cheong, S.-W., and Handley, M.F."Magnetization, EPR, Microwave Absorption and Specific Heat In Rare Earth Copper Oxides, R_2CuO_4." Accepted for publication by Phys. Rev. B. (1989)

b. Papers published in refereed journals:

Oseroff, S., Rao, D., Wright, F., Tovar, M., Vier, D. C., Schultz, S., Thompson, J. D., Fisk, Z., and Cheong, S.-W., "Observation of complex magnetic behavior in the Perovskite rare earth copper oxide systems, R_2CuO_4". Sol. St. Commun., 70, #12, 1159 (1989).(5 pages)

c. Books (and sections thereof) submitted for publication:

None

d. Books (and sections thereof) published:

None

e. Patents filed:

None

f. Patents granted:

None

g. Invited presentations at topical or scientific/technical society conferences:

None

h. Contributed presentations at topical or scientific/technical society conferences:

None

i. Honors, Awards/Prizes:

None

j. Graduate students and postdoctorals supported under the crp for the year ending 31 October 1988:

Joseph Anderberg, graduate student
Dr. David C. Vier, Postdoc/Researcher

CUMULATIVE BIBLIOGRAPHY, 1 MAY 1987 THROUGH 31 OCTOBER 1989

1. Vier, D. C., Oseroff, S. B., Salling, C. T., Smyth, J. F., Schultz, S., Dalichaouch, Y., Lee, B. W., Maple, M. B., Fisk, Z., and Thompson, J. D., "Precautions when interpreting EPR and dc magnetization measurements of high T_C $RBa_2Cu_3O_y$ phase superconducting materials", Phys. Rev. B.,**36** , #16, 8888 (1987), Rapid Communications. (3.5 pages) — RESEARCH ARTICLE

2. Hermann, A. M., Sheng, Z. Z., Vier, D. C., Schultz, S., and Oseroff, S. B., "Magnetization of the 120K TL-CA/Ba-Cu-O Superconductor", Phys. Rev. B, **37**, #16, 9742 (1988)(2.5 pages) — RESEARCH ARTICLE

3.* Oseroff, S., Rao, D., Wright, F., Tovar, M., Vier, D. C., Schultz, S., Thompson, J. D., Fisk, Z., and Cheong, S.-W., "Observation of complex magnetic behavior in the Perovskite rare earth copper oxide systems, R_2CuO_4". Sol. St. Commun., **70**, #12, 1159 (1989).(5 pages) — RESEARCH ARTICLE

4.** Oseroff, S.B., Rao, D., Wright, F., Vier, D.C., Schultz, S., Thompson, J., Fisk, Z., Cheong, S.-W., and Handley, M.F. "Magnetization, EPR, Microwave Absorption and Specific Heat In Rare Earth Copper Oxides, R_2CuO_4." Accepted for publication by Phys. Rev. B. (1989) — RESEARCH ARTICLE

*#3-This publication is to be counted as the first in this reporting year (11/1/88-10/31/89).

**#4 Preprint, note explaining significance of paper attached

ONR-N00014-87-K-0338, UCSD, S. SCHULTZ

PREPRINT - significance of paper

Complex magnetic properties of the rare earth copper oxides, R_2CuO_4 observed via measurements of the dc and ac magnetization, EPR, microwave magneto-absorption, and specific heat:

A. What was done: We grew good single crystals of the form R_2CuO_4, and $R_{2-x}L_xCuO_4$, (where R = Pr, Nd, Sm, Eu, or Gd, and L = Gd, Tb, or Dy). We then measured the temperature and magnetic field angle dependence of the :

1. dc magnetization,
2. ac susceptibility,
3. microwave magneto-absorption,
4. EPR (of Gd^{3+}), and
5. specific heat

B. The large body of data outlined in (A) above revealed many features. Some of these features we interpret as reflecting the strong antiferromagnetic exchange in the plane of the Cu-O moments, the subsequent 3D ordering at T ~ 270K, the presence of weak ferromagnetism and spin canting, at lower temperatures (< 20K) spontaneous spin reordering, and at still lower temperatures (< 6K) ordering of the R moments. Other features, while clearly related to the Cu moment spin system, such as the anisotropy of the Gd ion EPR field for resonance, or angular dependence of the weak ferromagnetism, are more complex and will require further effort to complete their explanation.

C. The importance of this work, is that the R_2CuO_4 materials studied, (for R = Pr,Nd, Sm or Eu) are the host materials which become superconductors when doped with Ce or Th. These are the new "electron" Cu-O superconductors. An important advantage of studying this class of copper-oxides is that they form a purely planar Cu-O structure, with no apical oxygens. Hence, it is felt that they will be more amenable to a fundamental understanding of the magnetic interactions which have been postulated to be the basis of the superconducting mechanism. In addition, even if further study should prove that there is no specific magnetic origin to the superconductivity, the many signatures of this complex magnetic system will be useful probes to provide discrimintaing tests of the alternate models that are proposed.

OFFICE OF NAVAL RESEARCH

FINAL TECHNICAL REPORT - CUMULATIVE

FOR

1 MAY 1987 - 31 OCTOBER 1989

FOR

CONTRACT NOOO14-87-K-0338

R&T NO. 414M013---01/87 FEB 18 (1114SS)

A NEW APPROACH TO UNDERSTANDING THE SEMICONDUCTOR SURFACE AND INTERFACES

DR. SHELDON SCHULTZ, PRINCIPAL INVESTIGATOR

UNIVERSITY OF CALIFORNIA, SAN DIEGO

DEPARTMENT OF PHYSICS, B-019

LA JOLLA, CALIFORNIA 92093

FINAL TECHNICAL REPORT - CUMULATIVE:

In the two prior Technical Reports (the first for the period May1 - October 31, 1987, and the second November 1 - October 31 1988) we outlined our progress toward utilizing electron paramagnetic resonance (EPR) as a probe of the silicon-metal interface. In prior experiments we had shown how EPR of the conducting electrons could be used to infer their transport properties. The specific property we sought to determine was the probability of electron transport across the interface as a function of interfacial preparation, metallic layer, etc. Toward this end we developed techniques for preparing special micron thin regions of highly P-doped silicon, and further techniques for preparing atomically clean surfaces of the silicon wafers introduced into a UHV system without the need for any high temperature processing. The wafers were then coated with a thin evaporated layer of Cu, Ag, Au, or Al.

The samples prepared, as just described, were then removed from the UHV system and examined in a variable temperature EPR spectrometer. From an analysis of the EPR linewidth data we are able to deduce the probability of an electron to tunnel across the interface under zero bias conditions. (this analysis assumes negligible spin relaxation at the interface, which will be further discussed below). From an extensive series of samples, which included Auger spectroscopy to quantify surface cleanliness, we were able to show that whereas electrons readily couple across when either a Cu, Au or even Al layer is used, they do not do so for Ag (Table 1). This is a very surprising result confirming the sensitivity of the process to the nature of the Si-metal bond at the interface, which confirms the inherent power of this approach.

In the preceding paragraph we emphasized that the interpretation of the data (but not the exsistence of the line broadening phenomon) depended on the assumption that the primary origin of the observed line broadening of conduction electron spins that tunnel from the P-doped silicon into the metal overlayer is from spin relaxation inside the metal, rather than at the discontinuity at the interface. In order to check this important assumption it is necessary to be able to prepare samples with metal thickness from the multi-monolayer down to the sub-monolayer level. Since each sample then has to be examined by EPR, it requires that the one have in-situ capability, as fractional monolayer samples cannot be withdrawn from the UHV environment. In our original proposal we explained how we would implement such an apparatus. Following our demonstration of the proof of EPR for studying the metal-semiconductor interface, we commenced construction of a dedicated UHV sample preparation system with in-situ EPR capability. This apparatus has been under active construction for a little over one year, and is very close to completion. During this period we have made some additonal measurements and checks on selected samples but, since the quality of sample and data that can be achieved in the new system will be so superior when compared to all samples made to date, we are now devoting all our effort to completing the final sub-assemblies.

We are gratified that our preliminary data (obtained with the samples which we made in the non-dedicated UHV system) has proved so interesting that our colleague Prof. Lu Sham and a new postoctoral visitor, Dr. V. Gomez, have commenced a detailed theoretical analysis of the spin transport across the silicon-metal interface, and the associated spin-flip cross-sections. The combination of the results of their theoretical effort with the data we will obtain with our new system should produce some exciting insights into the semiconductor surface-interface problem.

As discussed in the prior Technical Reports, we also became active in the study of the high T_c copper-oxide superconductors after the exciting discovery by Bednorz and Mueller. As specialists in EPR, our first impulse was to apply this tool to these materials. Of course, many others also tried EPR, and indeed there soon were reports of such signals. Unfortunately, these were due to spurious phases, and we published a paper clarifying this important point (see #1 on the cumulative publications list). We also developed the application of EPR for the detection of minute amounts of a

superconductor, even if enmeshed in a much larger amount of normal host material. In this manner we were able to detect superconductivity at the 10 nanogram level! Another feature of the technique is a sharp indication of the onset temperature, which was useful in our collaboration with Hermann, et al. in conjunction with their work on the Tl based highT_c materials. (see #2 on the cumulative publications list).

Most recently we have collaborated with Fisk and coworkers at Los Alamos for an extensive investigation of the magnetic properties of the host rare-earth copper-oxides (of the form R_2CuO_4), of the new " electron" superconductors. These Cu-O planar systems turn out to have quite complex magnetic properties which will require much more research to fully characterize and explain. However, we believe that in this process we will be able to clarify important questions, such as whether there really is a magnetic origin for the superconductivity. (see #3 and #4 on the cumulative publications list).

TABLE 1

Typical values of the probability of electron transport from P-doped Si into a metal contact as a function of surface phosphorus concentration for various metal-Si contacts.

Metal contact to P-doped Si Surface phosphorus concentration	Ag	Al	Au	Cu
3×10^{20}	$< 5 \times 10^{-5}$	2×10^{-4}	3×10^{-4}	8×10^{-4}
1×10^{20}	$< 5 \times 10^{-5}$	4×10^{-4}	5×10^{-4}	4×10^{-3}
3×10^{20}	$< 5 \times 10^{-5}$	3×10^{-3}	5×10^{-3}	1×10^{-2}

CUMULATIVE BIBLIOGRAPHY, 1 MAY 1987 THROUGH 31 OCTOBER 1989

1. Vier, D. C., Oseroff, S. B., Salling, C. T., Smyth, J. F., Schultz, S., Dalichaouch, Y., Lee, B. W., Maple, M. B., Fisk, Z., and Thompson, J. D., "Precautions when interpreting EPR and dc magnetization measurements of high T_c $RBa_2Cu_3O_y$ phase superconducting materials", Phys. Rev. B.,**36** , #16, 8888 (1987), Rapid Communications. (3.5 pages) RESEARCH ARTICLE

2. Hermann, A. M., Sheng, Z. Z., Vier, D. C., Schultz, S., and Oseroff, S. B., "Magnetization of the 120K TL-CA/Ba-Cu-O Superconductor", Phys. Rev. B, **37**, #16, 9742 (1988)(2.5 pages) RESEARCH ARTICLE

3. Oseroff, S., Rao, D., Wright, F., Tovar, M., Vier, D. C., Schultz, S., Thompson, J. D., Fisk, Z., and Cheong, S.-W., "Observation of complex magnetic behavior in the Perovskite rare earth copper oxide systems, R_2CuO_4". Sol. St. Commun., **70**, #12, 1159 (1989).(5 pages) RESEARCH ARTICLE

4. Oseroff, S.B., Rao, D., Wright, F., Vier, D.C., Schultz, S., Thompson, J., Fisk, Z., Cheong, S.-W., and Handley, M.F. "Magnetization, EPR, Microwave Absorption and Specific Heat In Rare Earth Copper Oxides, R_2CuO_4." Accepted for publication by Phys. Rev. B. (1989) RESEARCH ARTICLE